

LaRC-DEVELOPED CATALYSTS FOR CO₂ LASERS

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ABSTRACT

Pulsed CO₂ lasers have many remote sensing applications from space, airborne, and ground platforms. The NASA Laser Atmospheric Wind Sounder (LAWS) system will be designed to measure wind velocities from polar earth orbit for a period of up to three years. Accordingly, this and other applications require a closed-cycle pulsed CO₂ laser which necessitates the use of an efficient CO-O₂ recombination catalyst for these dissociation products which otherwise would degrade the laser operation. The required catalyst must not only operate at low temperatures but also must operate efficiently for long time periods.

The research effort at NASA LaRC has centered around development and testing of CO oxidation catalysts for closed-cycle, pulsed, common and rare-isotope CO₂ lasers. We have examined available commercial catalysts both in a laser and under simulated closed-cycle laser conditions with our efforts aimed toward a thorough understanding of the fundamental catalytic reaction and utilized these data to design and synthesize new catalyst compositions to better meet the catalyst requirements for closed-cycle pulsed CO₂ lasers. In this paper we report syntheses and test results for catalysts developed at Langley Research Center which have significantly better long-term decay characteristics than previously available catalysts and at the same time operate quite well under lower temperature conditions.

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INTRODUCTION

This report will outline the progress made at NASA Langley Research Center on the production, characterization, and testing of catalysts for the recombination of CO and O₂, the dissociation products of pulsed-discharge CO₂ lasers. The objective is to develop a catalyst with adequate activity and stability which would enable closed-cycle laser operation for periods of up to three years as required by the Laser Atmospheric Wind Sounder (LAWS) system.

Catalyst Requirements

Adequate activity implies that the catalyst have a high enough conversion efficiency to recombine CO and O₂ at a rate equal to or greater than its dissociation rate. For a pulsed-discharge CO₂ laser operating at 10 joules per pulse, dissociation rates have been estimated to be 10¹⁸ molecules per pulse. At 10 pulses per second (pps) the catalyst must have a recombination rate of 10¹⁹ molecules per second. Additionally, candidate catalysts must retain high conversion efficiency over a temperature range from ambient to 100°C and in low partial pressures of CO and O₂ without interference from other laser gas components--CO₂ in particular.

Adequate stability implies that the catalyst retain its recombination efficiency during the lifetime of operation as well as retain its structural integrity (i.e. must not crumble or dust). The LAWS system requires a lifetime of 10⁹ pulses. At 10 pps, this period is about 10⁸ seconds or three years. Consequently, the catalyst must show minimal decay in order to minimize the weight of catalyst required to provide the necessary recombination over the entire period of operation. To preserve the catalyst's structural integrity, it is necessary to develop a method of incorporating thin coatings of catalyst materials onto inert supports such as monoliths.

Because the laser signal is generated by CO₂, a gas present in the atmosphere, transmission of the laser signal can be diminished. In order to improve atmospheric transmission, the

LAWS system will use rare isotope CO_2 (C^{18}O_2). As a result, a candidate catalyst must operate with C^{18}O_2 without isotopic scrambling.

Catalysts Investigated

It has been shown that a combination of Pt and SnO_2 synthesized under the appropriate conditions is more active toward CO oxidation than either component alone.¹ It has also been shown that increased Pt loading increases catalyst activity for unsupported Pt/ SnO_2 . Addition of Pd further increases activity (Figure 1). The CO- O_2 recombination catalysts reported here are those available commercially and those produced at Langley Research Center (LaRC). These catalysts are mainly Pt/ SnO_2 or (Pt+Pd)/ SnO_2 , either supported or unsupported, with various promoters and dopants.

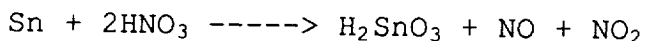
In the continued improvement of the catalyst, studies to optimize the Pt/ SnO_2 and Pt/Pd ratios for those yielding the highest activity are presented. A unique method of preparation whereby the Pt loading can be varied from 1% to 46% by weight of the Pt/ SnO_2 is used. In addition to the optimization studies, an investigation of the effect of various dopants and promoters on the activity of Pt/ SnO_2 is also presented.

In making the catalyst mechanically stable, as required by the LAWS system, methods of depositing the catalyst on inert supports such as silica spheres, silica gel, and monoliths are being developed. Although the support material is generally inert, support constituents such as water can affect the activity of Pt/ SnO_2 . As a result, the effect of water on catalyst activity will be discussed.

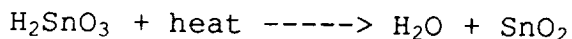
PROCEDURES

Catalyst Preparation

Preparation of the LaRC catalysts has been explained in detail earlier.² Briefly, tin is oxidized to metastannic acid via slow, nitric acid oxidation of 30-mesh tin granules.

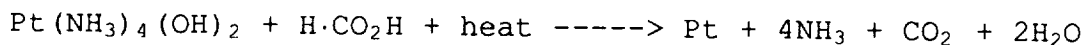


To ensure removal of excess nitric acid and water, the slurry is heated to dryness using a hotplate temperature of about 150°C. This heating converts metastannic acid to tin(II)oxide via dehydration.



For coating silica spheres or high surface-area silica gel with metastannic acid, tin is oxidized in the presence of the deaerated support.

Before deposition of platinum or palladium, the supported or unsupported substrate is deaerated in the presence of a solution of either tetraaminoplatinum(II)hydroxide or tetraaminopalladium-(II)nitrate. Platinum and palladium are then deposited via formic acid reduction.



Again the slurry is heated to dryness to remove excess water, formic acid, and the volatile byproducts. The preparation is completed by drying the catalyst in a convection oven in air at 150°C.

The above preparation has the unique characteristic of using volatile, chlorine-free reagents. The advantages of this are that the catalyst-poisoning chlorides are eliminated and that the excess reagents as well as their byproducts are volatile.

Catalyst Characterization

Catalysts are tested for their general activity, surface area, and water content. The general activity of catalyst samples is determined in plug flow reactors. Selected samples are tested in a system incorporating a pulsed-discharge CO₂ laser. For samples used in kinetic studies, a recycle reactor is used. All systems have been described in previous papers.^{3,4}

Activity screening. Each catalyst sample was screened in a plug flow reactor for its ability to recombine a stoichiometric test-gas mixture containing 1% CO and 0.5% O₂ in He with a 2% Ne internal standard. Gas mixtures were analyzed with an inline Shimadzu GC using a concentric column; the external column contains Activated Molecular Sieve for separating CO, Ne, O₂ and N₂, and the internal column contains a Porapak mixture for separating CO₂ from the other components. The peak areas of CO₂, Ne, O₂, N₂, and CO are determined via electronic integration using a Shimadzu CR3-A integrator. These areas are converted to concentrations by comparison to the 2% Ne internal standard.

Unless otherwise noted, a 150-mg sample of catalyst was used for screening. Each sample was reductively pretreated in situ at 125°C using a gas containing 5% CO in He with a 2% Ne internal standard flowing at 10 sccm. During pretreatment CO is oxidized to CO₂. When the CO₂ concentration was below 0.02% of the total analyzed sample, the catalyst sample was considered pretreated; this generally required 1 to 3 hours.

A general screening proceeds as follows. At preset times (ten consecutive then every four hours) 1-mL samples of test gas were analyzed for CO₂, O₂, and CO concentration. Next, the percent yield of CO₂, and the percent losses of O₂ and CO were calculated.

Surface area determination. The surface area of a catalyst sample is determined via the method of Brunauer, Emmett, and Teller (BET) using a Quantachrome Quantasorb instrument. The amount of sample used in determining the surface area ranges from 30 mg to 150 mg depending on the assumed surface area of the sample being tested.

Ignitions. A known weight of catalyst, about 100-mg, is heated in a porcelain crucible at 1000°C to constant weight. The first heating runs 60 minutes followed by at least two 30-minute heatings. The weight loss is assumed to be equal to the amount of water present in the catalyst.

RESULTS AND DISCUSSION

Because the purpose of this research is to improve upon the catalytic activity of previously produced catalysts, the discussion will focus on the relative changes in catalytic activity due to the addition of (1) other noble metals, (2) water, and (3) dopants.

Comparative Catalyst Study

Some of the earliest produced LaRC, CO-O₂ recombination catalysts were compared with those commercially available. The Pt loading of the LaRC-prepared catalysts is shown below.

	LaRC 1 and 1A	LaRC 2	LaRC 3	LaRC 6
Wt % Pt in Pt/SnO ₂	46.0	1.03	3.01	5.84
Wt % Pt in Pt/SnO ₂ /SiO ₂	15.5	0.206	0.622	1.237
% Area coverage by Pt	33.3	0.367	1.121	2.23

Figure 2 shows the activity--under stoichiometric test gas flow--of the above catalysts as well as those prepared by Engelhard (Eng), General Motors (GM), and Teledyne (TD). Activity is defined as sccm of CO₂ produced per minute per gram of catalyst. The GM and TD catalysts have the lowest activity. At elevated temperatures and in air, where excess oxygen is available, however, these have higher activities. These catalysts then are unsuited for a closed-cycle laser application.

The Engelhard catalyst (2% Pt/SnO₂) shows similar activity to LaRC 2 yet the latter uses a lower Pt loading making it more economical. LaRC 1 and 1A show higher activity than the others tested, but the excessive weight of Pt used makes it less cost effective. It may be necessary, however, to use such high loadings to achieve the activity per unit weight of catalyst required by the LAWS system.

Catalyst Optimization Study

Optimization of Pt/SnO₂. In order to determine the best Pt/SnO₂ ratio, compositions of Pt/SnO₂ supported on SiO₂ spheres and varying from 1% to 46% Pt by weight were prepared by the method discussed earlier. Their Pt loading on a weight percentage basis is shown in Table I; surface areas are indicated where available.

The catalysts were tested for activity in a plug-flow reactor under stoichiometric test gas conditions. The results of the tests are shown in Figure 3 as sccm of CO₂ produced per minute per gram of catalyst. The bimodal distribution indicates that peaks in activity exist for catalysts containing approximately 17% or 39% Pt by weight, the higher of these two peaks being for the 17% Pt/SnO₂. These results indicate that a Pt loading around 17% by weight provides the best activity under these conditions.

Figure 4 show the slope (% CO₂ yield/time) for the Engelhard and LaRC catalysts containing 24%, 32%, 39%, and 46% Pt by weight. Smaller negative slopes indicates better decay characteristics zero slope indicating no decay. Accordingly, sample 32-B, 39-B, and 46-B show less than half the decay rate of the Engelhard, and sample 24-B shows about 1/10th the decay rate of the Engelhard. Because the lower loadings (3%, 11%, and 17%) had nonlinear slopes between 5,000 and 10,000 minutes, they were not considered here.

Optimization of Pt/Pd. In order to determine the optimum Pt/Pd ratio, silica gel supported (Pt+Pd)/SnO₂ samples with Pd loadings from 1% to 19.5% by weight were prepared and tested in a plug flow reactor. To minimize differences due to sample preparation, samples were prepared from the same lot of silica gel-supported Pt/SnO₂. The Pd was added in a separate step. As a result, the atom ratio of Pt/SnO₂ is constant for all samples at 19.5%, and only the Pt/Pd ratio varies. Note that one sample contains no Pd.

Figure 5 shows the percent yield of CO₂ as a function of time for the aforementioned samples. The general shape of the curves is nearly the same indicating that the decay rate is approximately equal for each catalyst. The activities vary only slightly, but

significantly nonetheless. The lower loadings of Pd (1% and 2% by weight) decreased catalyst activity relative to the activity of the standard catalyst, Pt/SnO₂, whereas higher loadings (10% and 19.5% by weight) had little effect. A significant increase in activity, however, was observed for a Pd loading of 5% by weight; this is equal to 1/2 the amount of Pt on an atomic basis.

Figure 6 shows the sccm of CO₂ per gram of catalyst formed at 20000 minutes for various Pd compositions. Again, the graph shows an approximate 30% decrease in activity for the lower loadings of Pd, while showing little change in activity for the higher loadings. Notably, the 5% loading of Pd showed about 33% greater activity than the standard suggesting that approximately 5% Pd is the best loading for (Pt+Pd)/SnO₂ catalyst with high Pt loading.

Catalyst-Support Interaction

The effect of water on the recombination efficiency of Pt/SnO₂ catalysts has been extensively investigated at NASA Langley Research Center.^{5,6} Thermogravimetric analysis (TGA) of the Engelhard sample shows a weight loss of 3.73% when heated to 850°C. It is likely that the weight loss is due mostly to water. It has been shown that the initial dip in activity of the 2% Pt/SnO₂ (Engelhard) catalyst is alleviated if small amounts of water vapor are added to the pretreatment gas (Figure 7).

Silica gel support. Because of the importance of water to the activity of Pt/SnO₂ catalysts, high surface area silica gel was used to support some of the LaRC formulations. Silica gel, aside from its inert support properties, is a desiccant. The vapor pressure of water over silica gel is dependent on both the temperature and the concentration of water in the silica gel (Table II). Consequently, the amount of water reaching the catalyst can be controlled. The desiccant effect of silica gel might also be of practical utility in the laser where it could control the water vapor level so as not to reduce laser power.

The first silica gel-supported Pt/SnO₂ catalyst contained 7% Pt, 42% SnO₂, and 51% SiO₂. Figure 8 shows the percent yield of CO₂ for this catalyst for 35,000 minutes. At 85°C the catalyst

gave 100% yield indicating a potentially higher activity. The temperature was lowered in order to observe a measurable activity. After stabilization at 50°C, the percent yield remained around 90%.

A long-term test of this catalyst--106 days--near ambient temperature is shown in Figure 9. The graph shows that the catalyst's activity is susceptible to temperature fluctuations. Notably, the catalyst efficiency ranged from 90% to 65% loss of CO over the 106 days. This results in an extrapolated half-life of 228 days (Figure 10).

Effect of water on silica gel-supported Pt/SnO₂. To determine how this catalyst's activity varies under different concentrations of water, a known weight of deionized water was added to a known weight of catalyst. The quantity of water was incremented from sample to sample until saturation was reached. Two samples were prepared by dehydrating the catalyst in air in a convection oven either with or without a desiccant of magnesium perchlorate. The same amount of catalyst on a dry basis was tested. Two samples were tested simultaneously against the standard catalyst, no water added or removed. Figure 11 shows the reproducibility of activity for the standard catalyst.

Figure 12 shows the percent yield of CO₂ as a function of water content at 12,000 minutes of exposure to test gas. Neither the decay rate nor the catalyst activity was significantly affected by dehydrating or hydrating the catalyst. The activity remains relatively constant over the range of water compositions until saturation is reached at which point a 35% decrease in activity was observed. This result demonstrates that using silica gel as a support minimizes changes in activity due to water which could be advantageous for closed-cycle CO₂ lasers where an excess of water can significantly reduce the laser's power.

Monolithic supports. Supporting the catalyst formulations on a rugged, high surface-area, monolithic structure is currently under investigation at LaRC. One candidate monolith being investigated is a Cordierite monolith made by Dow Corning (Figure 13). It measures 3 inches in diameter and 0.5 inches thick, has

400 cells per square inch, and has a BET surface area of less than 1 m²/g. A method of increasing the surface area to over 200 m²/g and leaving a silica gel-like framework has been developed. The method involves leaching the monolith in dilute nitric acid to remove the Mg and Al. Sufficient structural integrity is retained during the process.

Effect of Promoters on Catalyst Activity

Chromium as a promoter. Figure 14 shows the percent yield of CO₂ over a 14,000 minute period for a Pt/SnO₂ catalyst both with and without Cr. The added Cr did not affect the decay characteristics and decreased the activity slightly.

Acidic oxide promoters. It is generally known that acidic oxides have little affinity for CO₂, the degree of affinity being inversely related to the oxide's acidity. In order to increase the rate of release of CO₂ and minimize CO₂ retention on the catalyst, a series of samples of Pt/SnO₂ with acidic oxide promoters were made and tested for catalytic activity. Oxides of antimony, arsenic, and phosphorus were chosen. Figure 15 shows the percent yield of CO₂ for 15,000 to 20,000 minutes. Relative to the catalyst containing no promoters three observations can be made: (1)the antimony oxide severely reduced the conversion efficiency; (2)the phosphorus oxide reduced the conversion efficiency by about 17% but did not affect the decay rate; and (3)the arsenic oxides increased the decay rate of the catalyst. For the amounts used, these oxides are not promising promoters.

Another oxide promoter whose identity is presently proprietary has been shown to enhance catalyst activity in quantities as low as 1% by weight, but decrease activity in higher amounts, 5% by weight (Figure 16).

SUMMARY

During the course of research at LaRC, catalysts exhibiting higher activity and lower decay rates than catalysts made previously have been prepared. An inherently clean method of preparing catalysts has been developed. Some noble-metal reducible oxide catalysts--Pt/SnO₂ in particular--have a demonstrated high activity at ambient temperatures. Traces of water appear to be necessary. Optimum loadings for Pt and Pd for Pt/SnO₂ and (Pt+Pd)/SnO₂ catalysts have been determined.

A method of supporting some of the LaRC catalyst formulations on silica spheres and high surface area silica gel has been developed. Investigation of monolithic structures for catalyst support is underway. A method of increasing the surface area of Cordierite monoliths from less than 1 m²/g to greater than 200 m²/g and leaving a silica gel-like structure has been developed.

Future efforts will focus on (1) adapting the catalyst for use with rugged high-porosity monolithic supports; (2) further reducing the long-term decay in the catalyst; (3) testing and modeling long-term behavior for reliable performance prediction for missions of interest; and (4) investigating alternative catalysts for higher conversion efficiency.

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6. Upchurch, Billy T.; Schryer, David R.; Wood, George M.; Hess, Robert V.: Development of CO Oxidation Catalysts for the Laser Atmospheric Wind Sounder (LAWS), SPIE Proc., vol. 1062, 287-293, 1989.

Table I. LaRC Catalysts on 10 Micron Sphere Support

<u>Catalyst Sample</u>	Pt as percent of:		<u>BET Area m²/gram</u>
	<u>Total Mass</u>	<u>Coating Only</u>	
1 B	0.21	1.01	
3 B	0.63	3.03	
6 B	1.24	5.90	
11 B	2.45	11.0	143
17 B	4.02	17.1	157
24 B	5.92	23.7	134
32 B	8.73	32.1	131
39 B	11.4	38.9	
46 B	14.7	46.0	

Table II. Vapor Pressures of Silica Gel at 40°C

<u>% Water</u>	<u>Vapor Pressure, mm Hg</u>
0.75	0.0076
1.0	0.013
1.2	0.050
3.0	0.175
6.0	0.505
12.0	1.500
20.0	2.500

Source: W. R. Grace Co.; Davidson Silica Gel

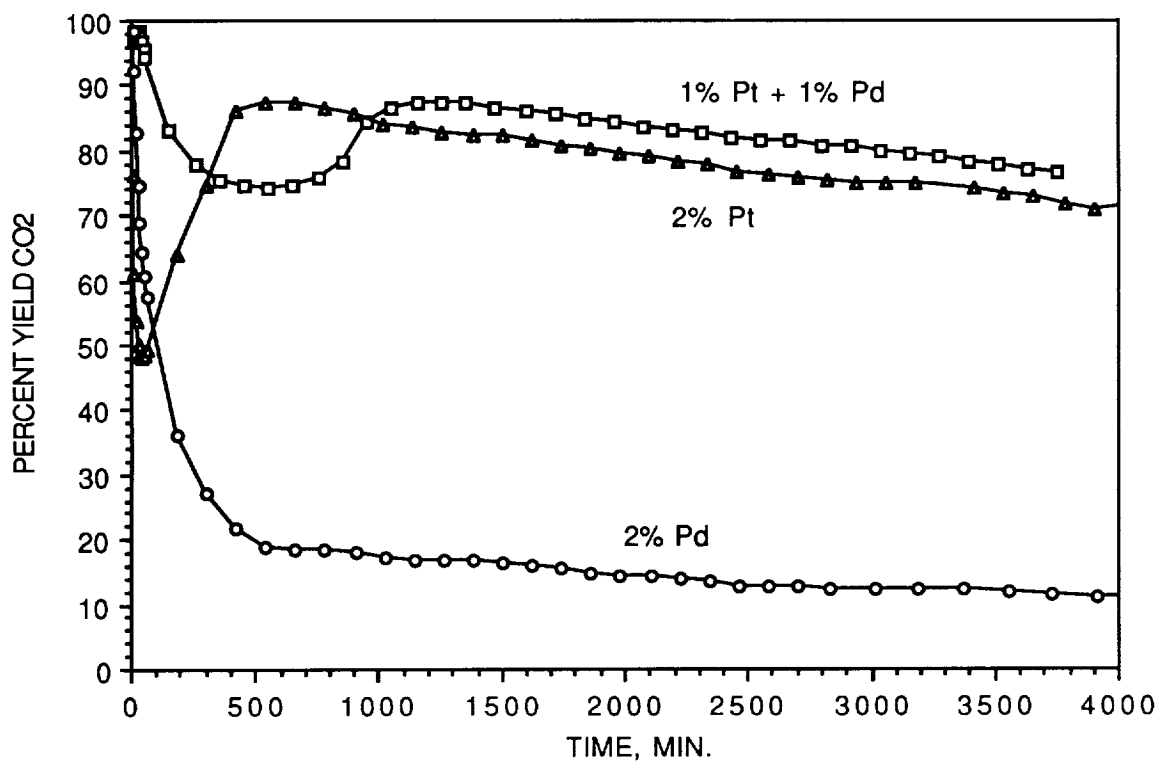


Figure 1. Comparison of Pt/SnO₂, Pd/SnO₂, and (Pt+Pd)/SnO₂ catalysts

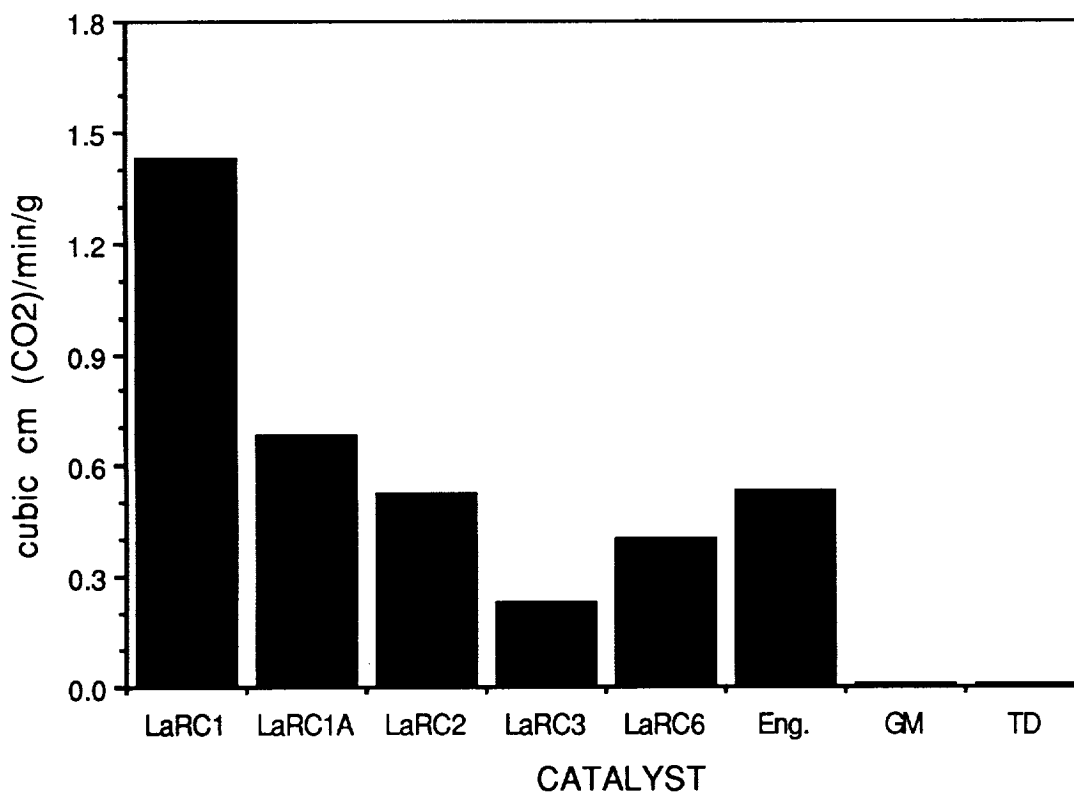


Figure 2. Comparison of commercial and LaRC catalysts

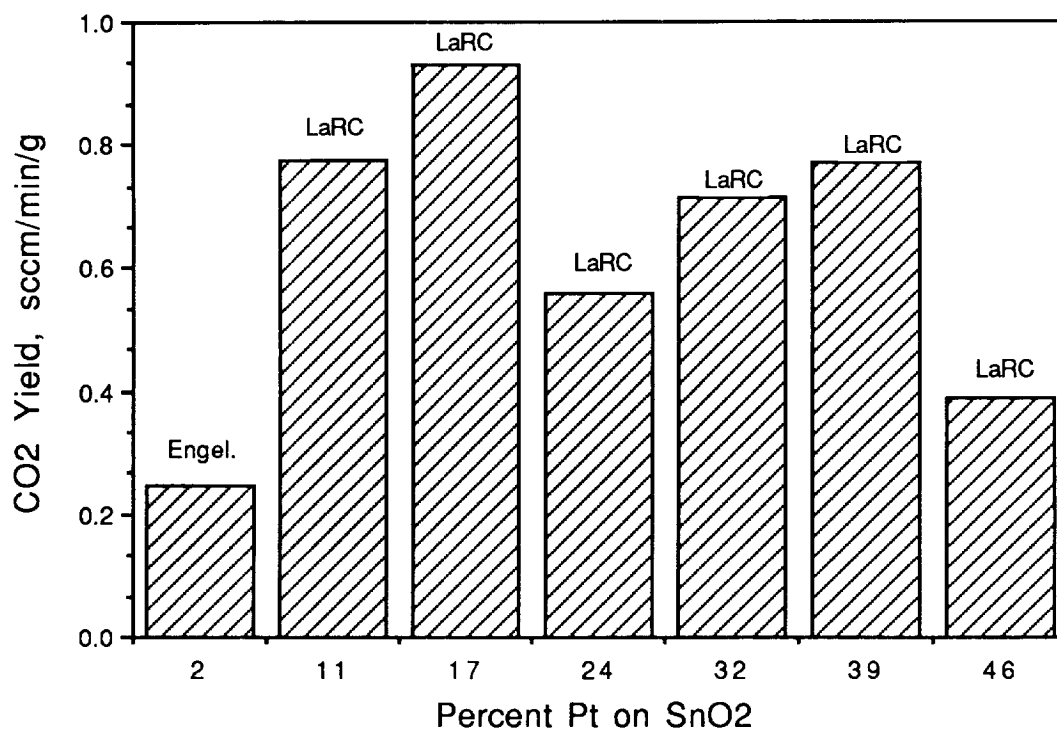


Figure 3. Effect of Pt loading on the activity of Pt/SnO2 catalysts

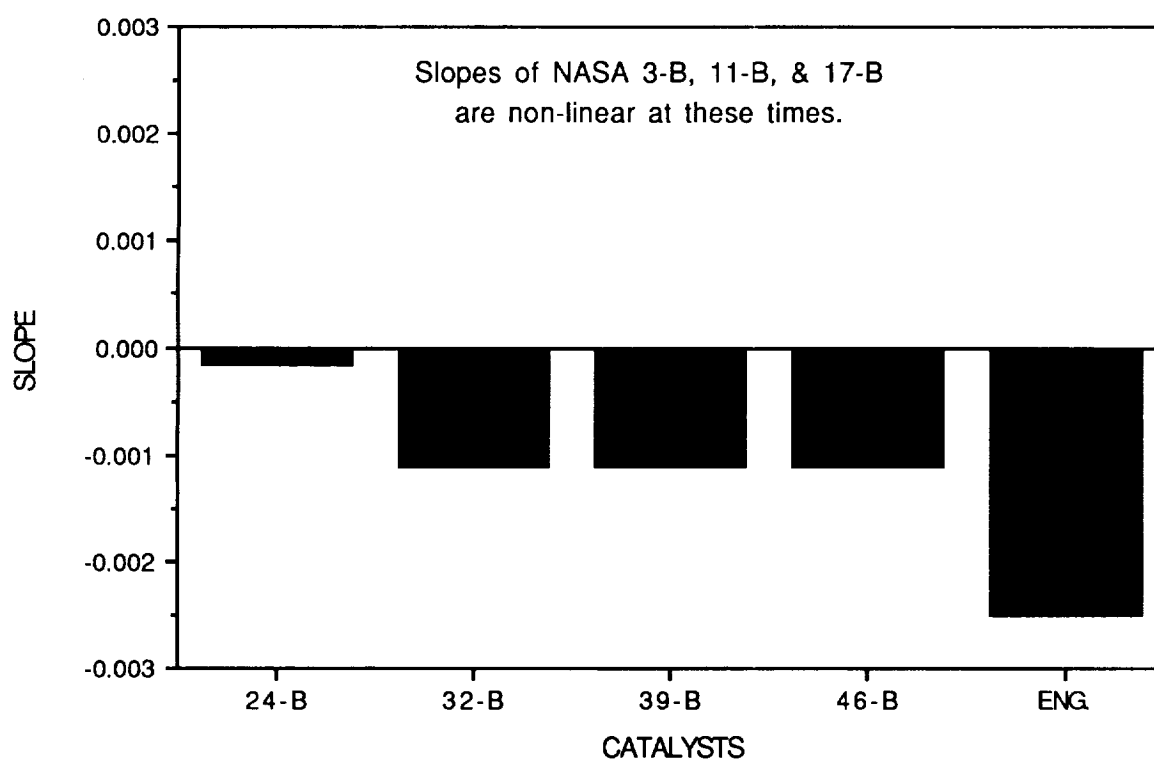


Figure 4. Slope of the activity curve between 5,000 and 10,000 minutes for some Pt/SnO2 catalysts

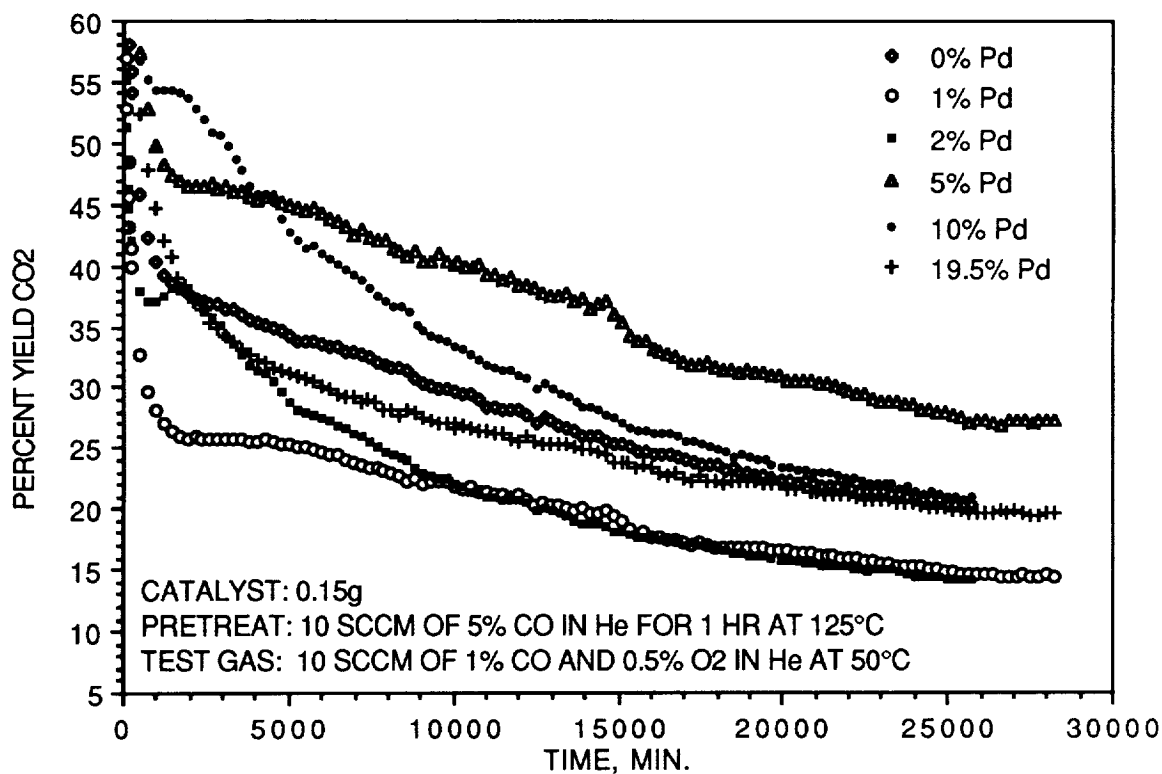


Figure 5. Effect of Pd loading on the activity of silica gel-supported (Pt+Pd)/SnO₂ catalysts

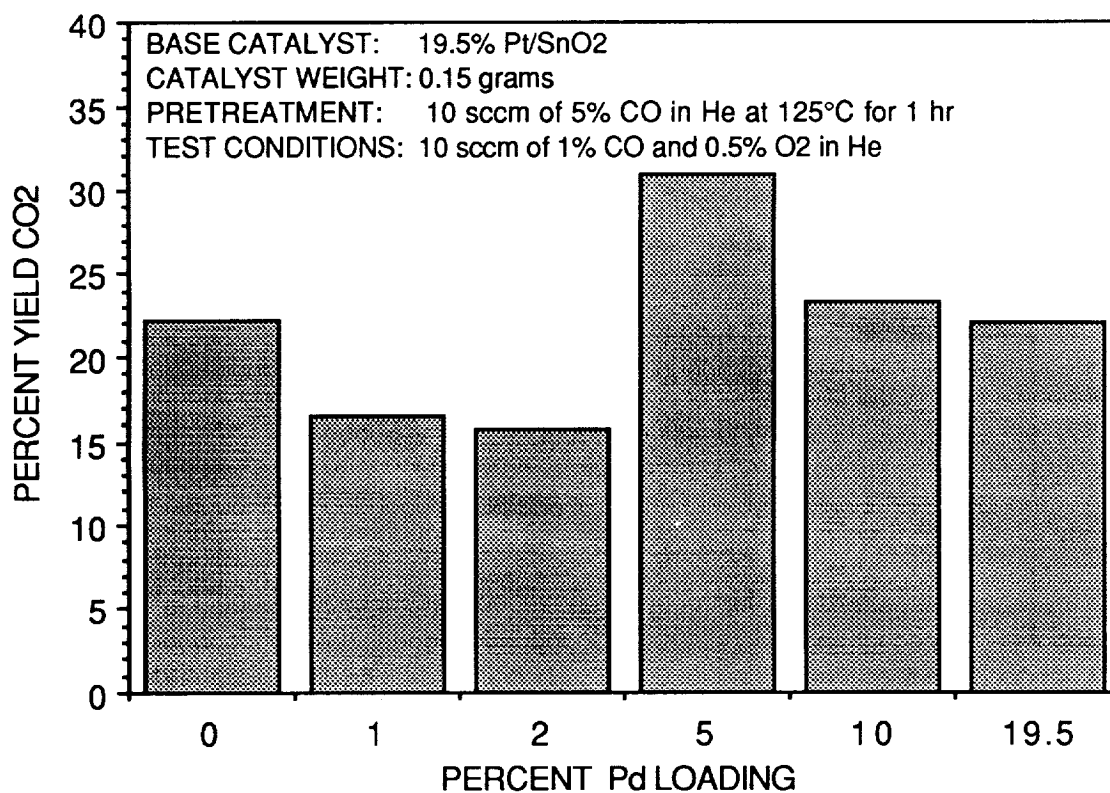


Figure 6. Activity at 20,000 minutes of some (Pt+Pd)/SnO₂ catalysts

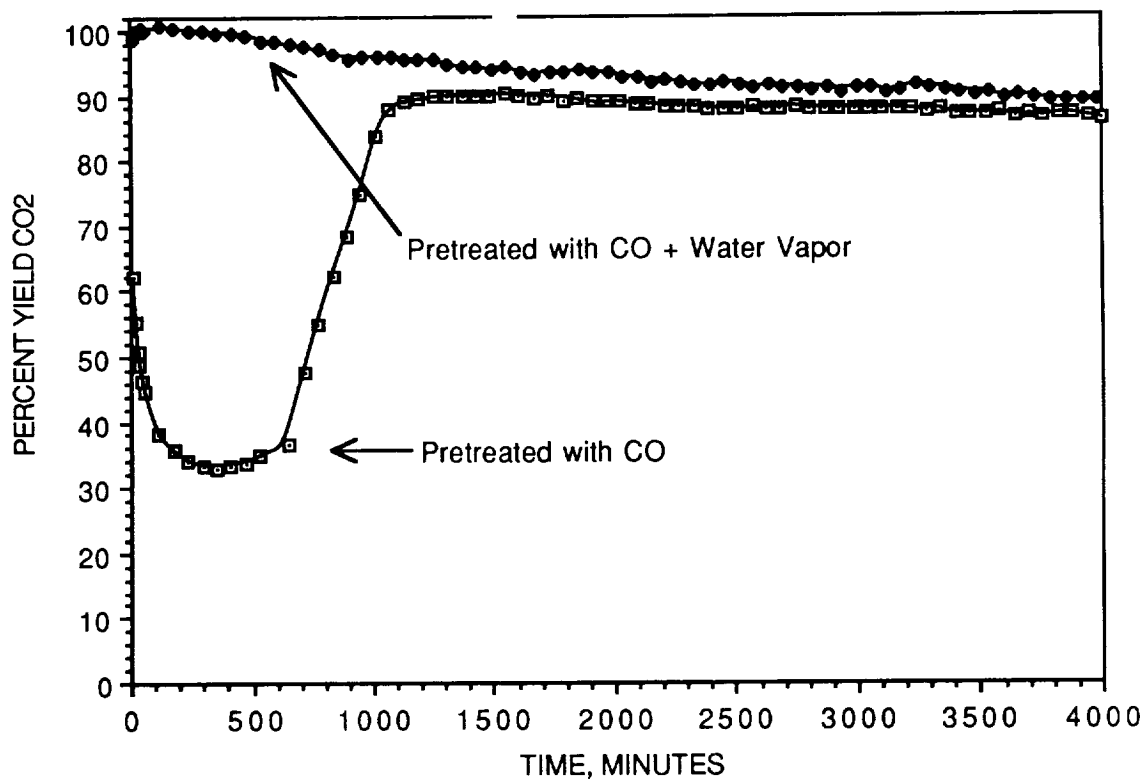


Figure 7. Effect of water vapor during pretreatment on the activity of 2% Pt/SnO₂

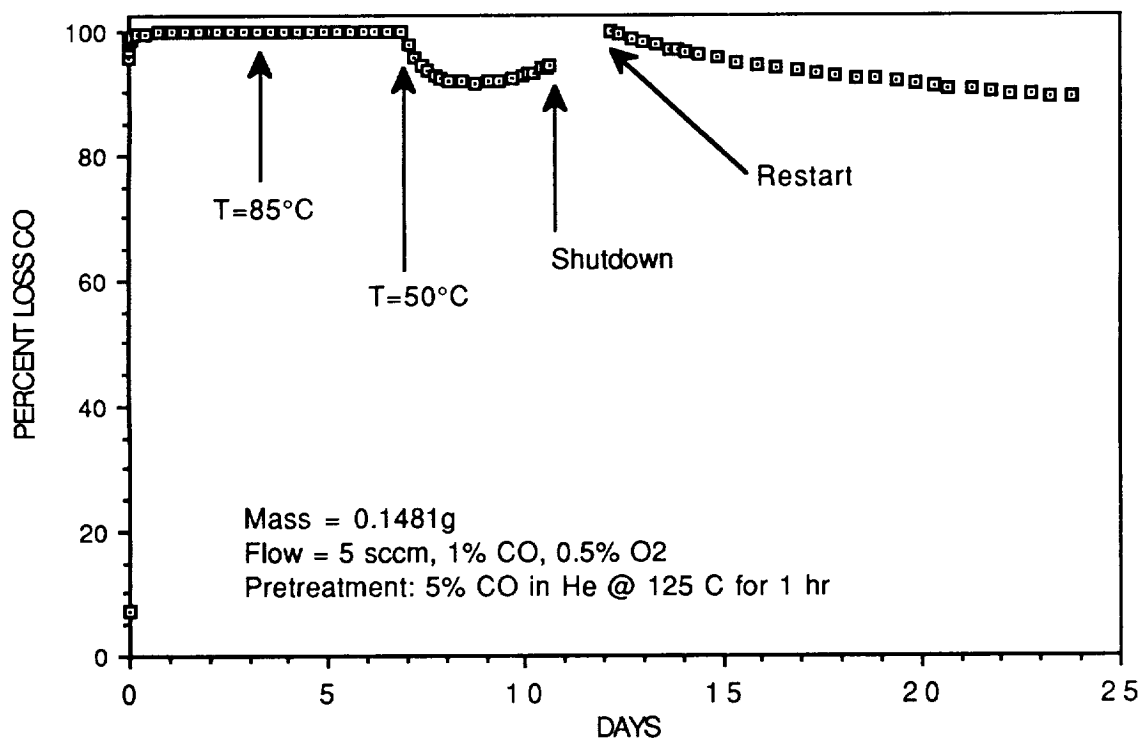


Figure 8. Activity of LaRC 1C, a silica gel-supported Pt/SnO₂ catalyst

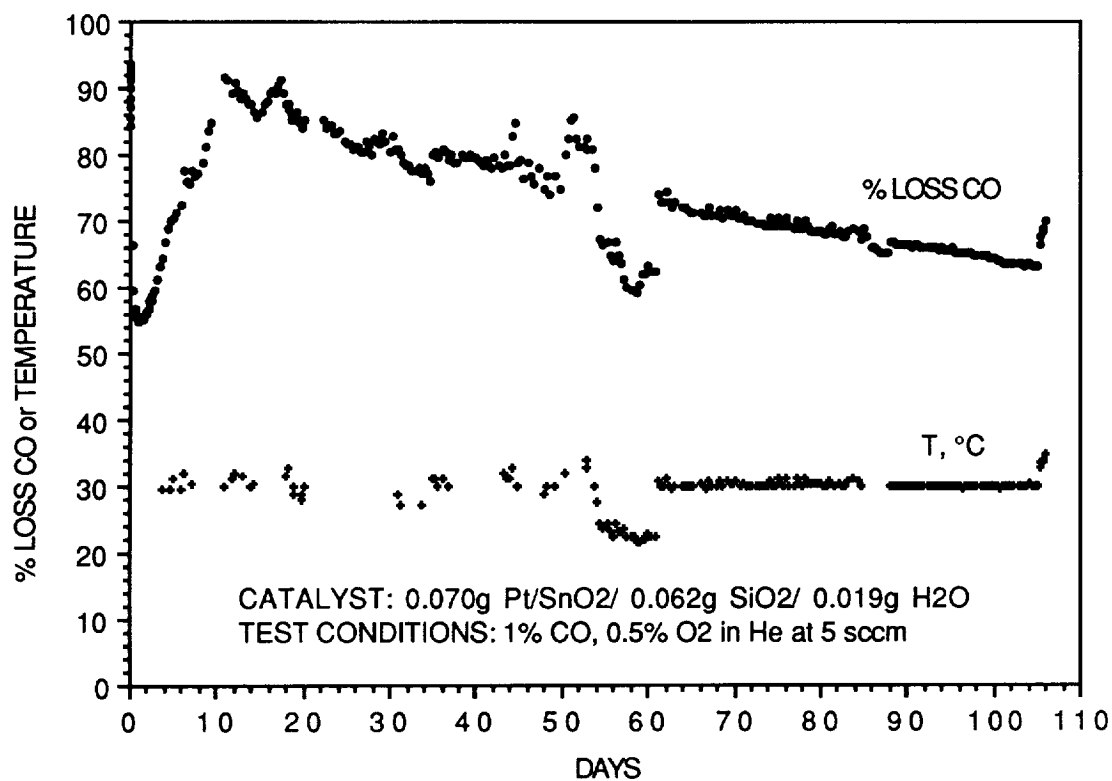


Figure 9. Long-term activity of LaRC 1C at near ambient temperature

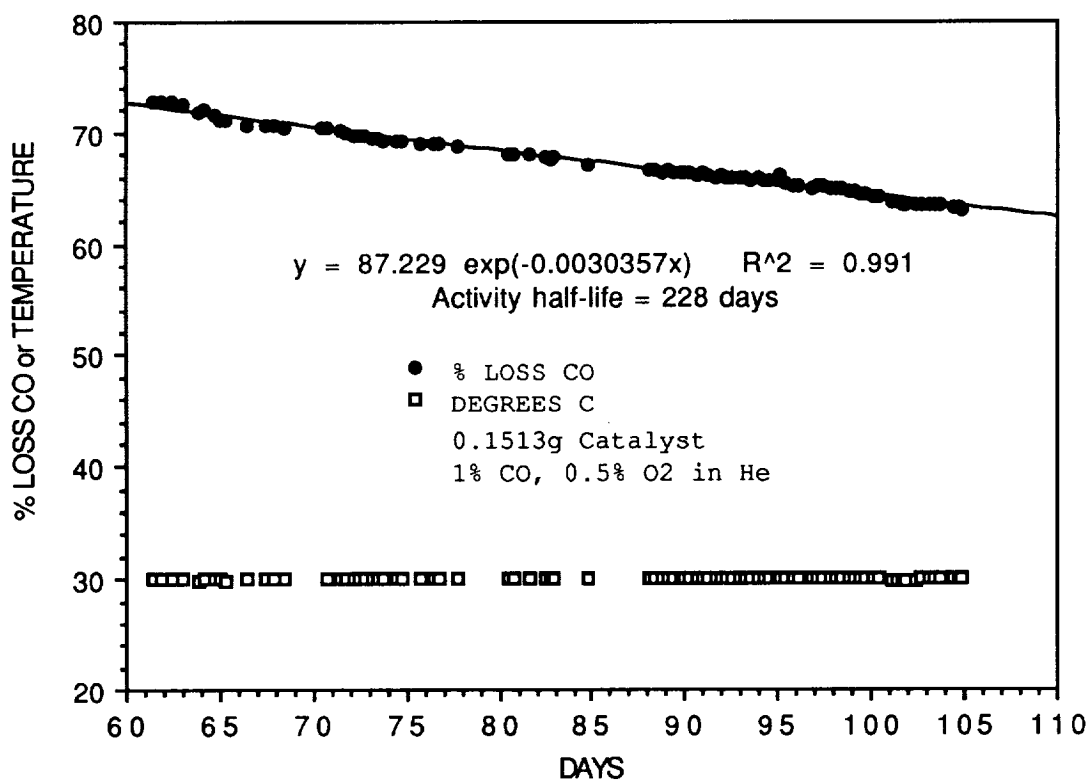


Figure 10. Extrapolated half-life of LaRC 1C

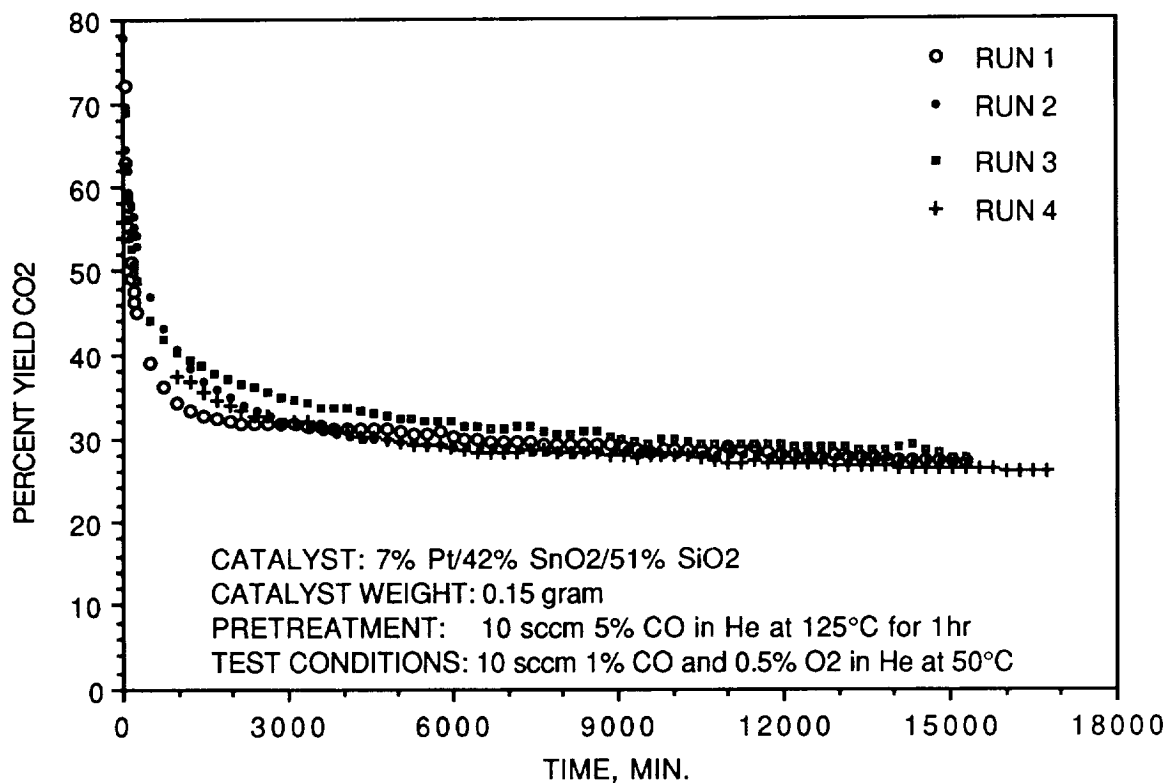


Figure 11. Reproducibility in activity for repeated screening tests of LaRC 1C,3

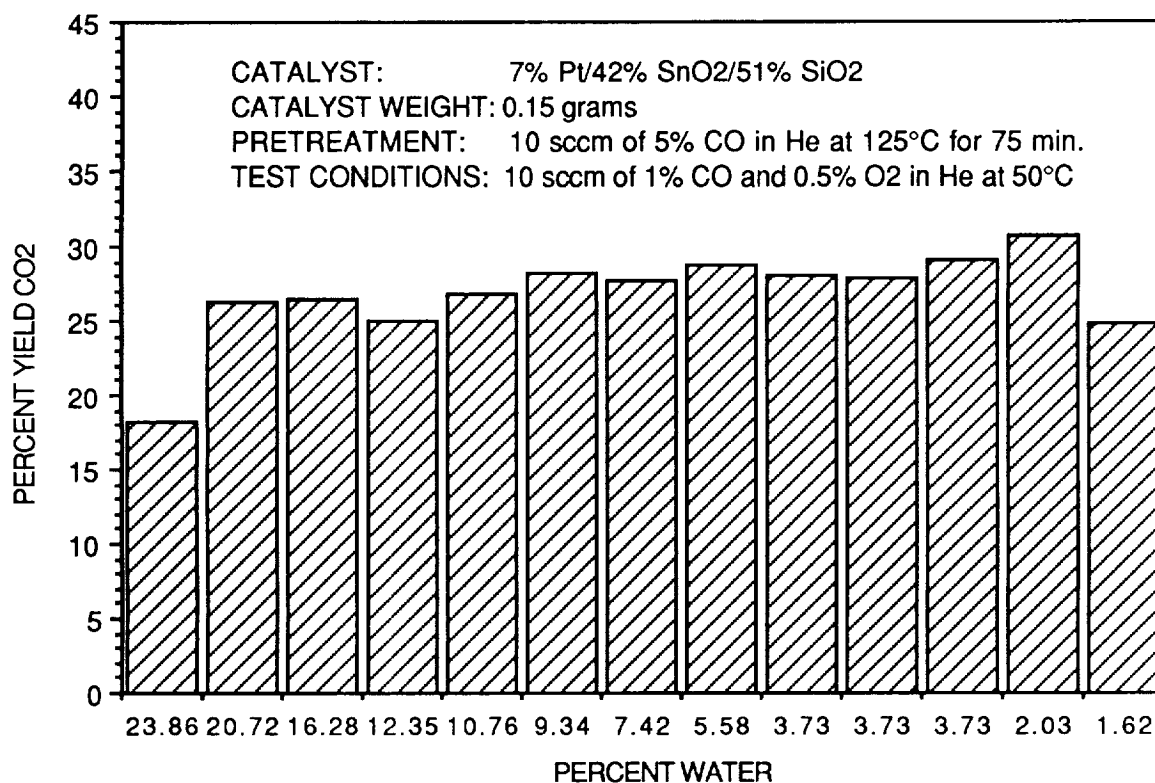
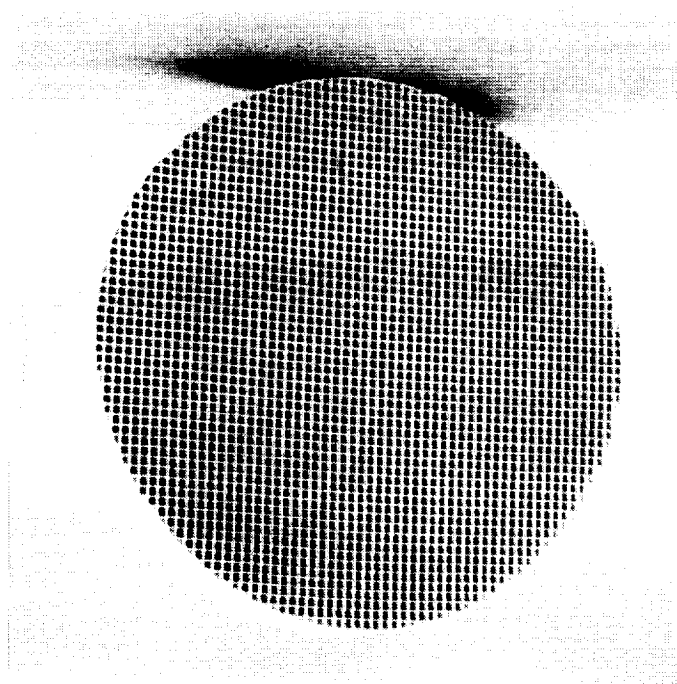


Figure 12. Effect of water on the activity of LaRC 1C, a silica gel-supported Pt/SnO₂ catalyst

Figure 13. Cordierite honeycomb monolith; 3 inches in diameter by 1/2 inch thick, 400 cells per square inch



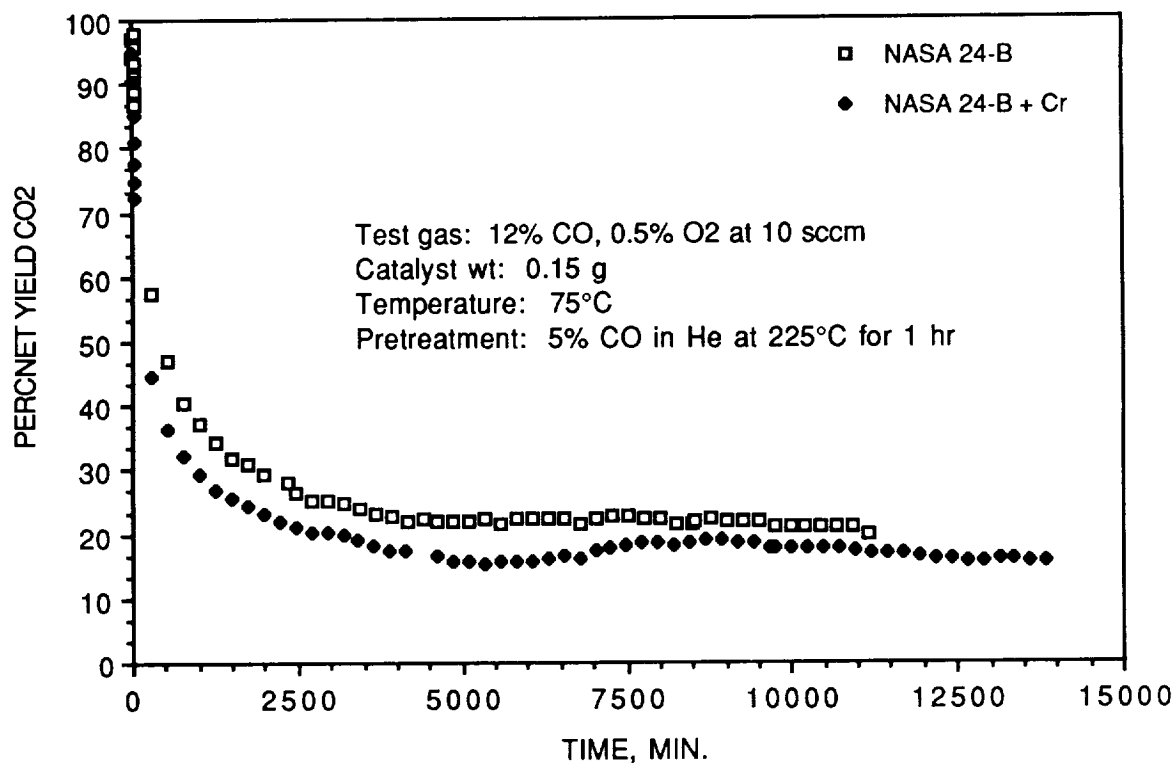


Figure 14. Comparison of LaRC 24B with and without Cr as a promoter

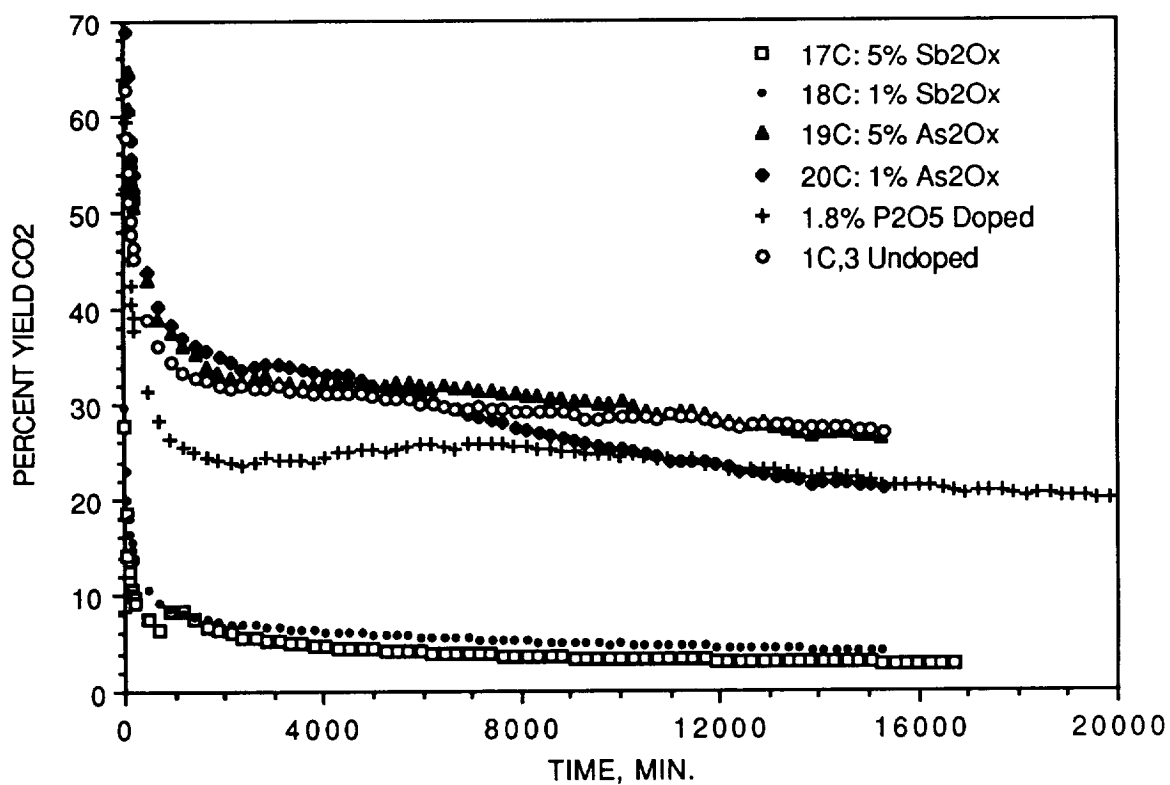


Figure 15. Comparison of activities for silica gel-supported Pt/SnO₂ doped with various acidic oxides

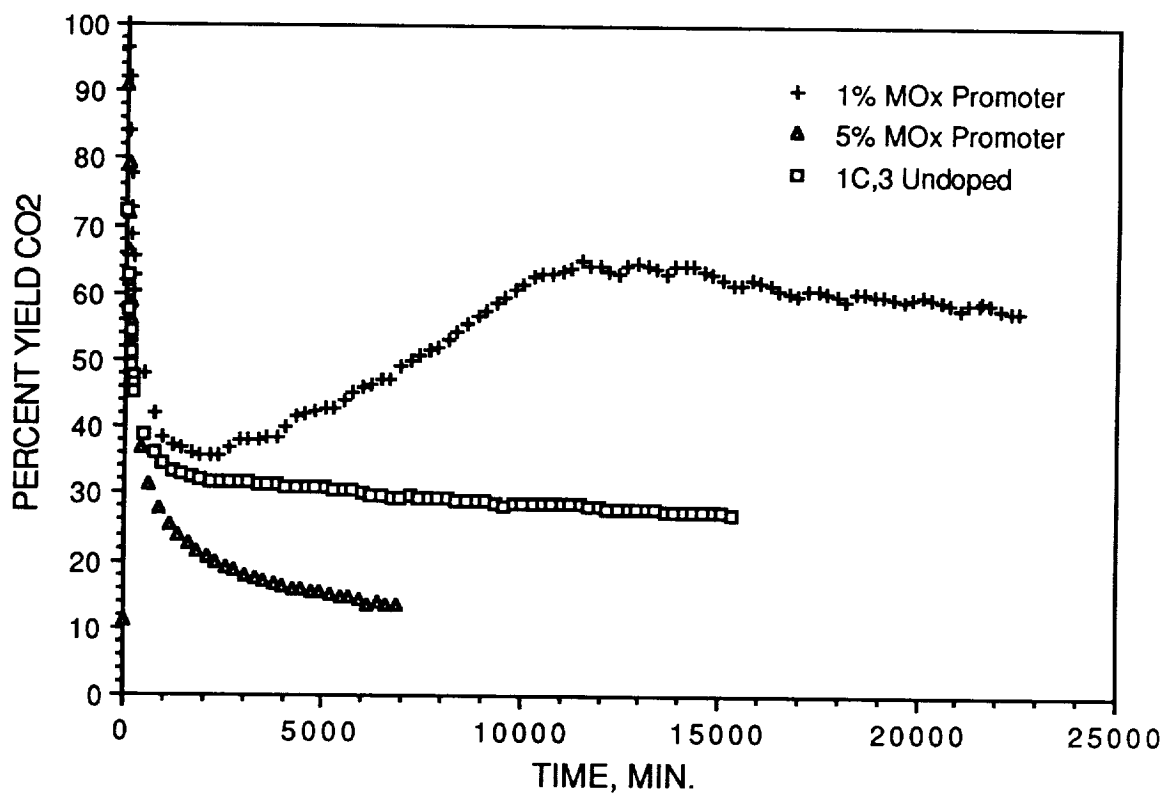


Figure 16. Comparison of activities for silica gel-supported Pt/SnO₂ with those doped with an acidic oxide promoters